

WD-A108 517

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THE ELECTRICAL PROPERTIES OF  $\text{NaSCuS}_4$ , A MIXED-VALENCE ONE-DIME--ETC (1)

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N00014-75-C-0756

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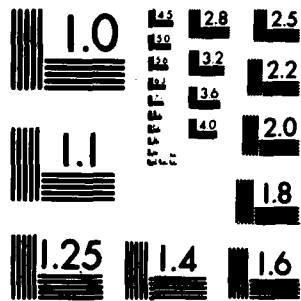
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REPORT DOCUMENTATION LEVEL		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
23 (Vermont; 18 (North Carolina)	AD-1108517	6
4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED	
The Electrical Properties of $\text{Na}_3\text{Cu}_4\text{S}_4$ , A Mixed-Valence One-Dimensional Metal.	Technical Report	
7. AUTHOR(s)	6. PERFORMING ORG. REPORT NUMBER	
Peplinski, D.B. Brown, T. Watt, W.E. Hatfield, and P. Day (Oxford)		
9. PERFORMING ORGANIZATION NAME AND ADDRESS	8. CONTRACT OR GRANT NUMBER(s)	
Department of Chemistry Department of Chemistry University of Vermont University of N. Carolina Burlington, VT 05405 Chapel Hill, NC 27514	N00014-75-C-0756 (Vermont) N00014-76-C-0816 (North Carolina)	
11. CONTROLLING OFFICE NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
Office of Naval Research Department of the Navy Arlington, Virginia 22217	2 -	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	12. REPORT DATE	
	Dec. 1, 1981	
	13. NUMBER OF PAGES	
	15	
	15. SECURITY CLASS. (of this report)	
	Unclassified	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report)		
This document has been approved for public release and sale; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
TIC LECTE DEC 14 1981		
18. SUPPLEMENTARY NOTES		
To be published in Inorganic Chemistry		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Mixed-valence, conductivity, one-dimensional metal, structure, copper sulfide sheet structure, infinite chain		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
<p>Four probe electrical conductivity measurements from 15-300K demonstrate that the mixed-valence compound <math>\text{Na}_3\text{Cu}_4\text{S}_4</math> is metallic. Measurements on single crystals reveal that the conductivity is highly anisotropic, with enhanced conductivity parallel to the crystal needle axis, corresponding to pseudo one-dimensional <math>[\text{Cu}_4\text{S}_4]^{3-}</math> columns in the structure. For single crystals, <math>\sigma</math> increases from <math>15000 \Omega^{-1} \text{cm}^{-1}</math> at 300 K to <math>300000 \Omega^{-1} \text{cm}^{-1}</math> at 15K. A small, temperature independent magnetic susceptibility is consistent with metallic behavior. Diffuse reflectance spectra support the formulation of this compound</p>		

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EDITION OF 1 NOV 69 IS OBSOLETE  
S/N 0102-LP-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

8112 11100

1/15000 ohm cm  
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1/300,000 ohm cm

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→ as a Class III B mixed-valence  $S^{2-}/S^{-}$  solid. ^

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Editor	
Reviewer	
Classification	
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Availability Codes	
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OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0756

Task No. NR 356-593

TECHNICAL REPORT NO. 23

(Vermont)

Contract N00014-76-C-0816

Task No. NR 053-617

TECHNICAL REPORT NO. 18

(North Carolina)

The Electrical Properties of  $\text{Na}_3\text{Cu}_4\text{S}_{41}$

A Mixed-Valence One-Dimensional Metal

by

Zbigniew Peplinski, David B. Brown, Timothy Watt,  
William E. Hatfield, and Peter Day.

Prepared for publication

in

Inorganic Chemistry

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December 1, 1981

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The Electrical Properties of  $\text{Na}_3\text{Cu}_4\text{S}_4$ , a  
Mixed-Valence One-Dimensional Metal

by

Zbigniew Peplinski,<sup>1a</sup> David B. Brown,<sup>\*1a</sup> Timothy Watt,<sup>1a</sup>  
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Abstract

Four probe electrical conductivity measurements from 15-300K demonstrate that the mixed-valence compound  $\text{Na}_3\text{Cu}_4\text{S}_4$  is metallic. Measurements on single crystals reveal that the conductivity is highly anisotropic, with enhanced conductivity parallel to the crystal needle axis, corresponding to pseudo one-dimensional  $[\text{Cu}_4\text{S}_4]_{\infty}^{3-}$  columns in the structure. For single crystals,  $\sigma_{\parallel}$  increases from  $15000 \Omega^{-1}\text{cm}^{-1}$  at 300 K to  $300000 \Omega^{-1}\text{cm}^{-1}$  at 15 K. A small, temperature independent magnetic susceptibility is consistent with metallic behavior. Diffuse reflectance spectra support the formulation of this compound as a Class III B mixed-valence  $\text{S}^{2-}/\text{S}^{-}$  solid.

## Introduction

In 1952 Rudorff, Schwarz, and Walter reported a remarkable series of mixed-valence solids.<sup>2</sup> Heating mixtures of copper, sulfur and alkali carbonates in a muffle furnace to temperatures of 700-1000°C gave shiny blue-black solids with compositions indicating the formal incorporation of one copper(II) ion and 2, 3 or 7 copper(I) ions - e.g.,  $\text{Na}_2\text{Cu}_3\text{S}_3$ ,  $\text{KCu}_4\text{S}_3$ , and  $\text{K}_3\text{Cu}_8\text{S}_6$ . Recently, several isostructural analogues of  $\text{KCu}_4\text{S}_3$  have been reported.<sup>2,3,4</sup> Intrigued by the original report of high electrical conductivity in these materials, we initiated studies of their structural, electrical, and magnetic properties, and we have recently demonstrated<sup>5</sup> that  $\text{KCu}_4\text{S}_3$  is a two-dimensional metal. In contrast to the plate-like crystals of the two-dimensional  $\text{KCu}_4\text{S}_3$ ,  $\text{Na}_2\text{Cu}_3\text{S}_3$  was reported to form needle-like crystals. Although crystal morphology is not a perfect guide to structure, it seemed possible that  $\text{Na}_2\text{Cu}_3\text{S}_3$  might be one-dimensional, both structurally and electrically. While our studies of this material were in progress. Burschka reported<sup>6</sup> its structure and demonstrated that its actual composition is  $\text{Na}_3\text{Cu}_4\text{S}_4$ , nominally a Cu(I,I,I,II) mixed-valence compound. The structure consists of one-dimensional columns, with  $[\text{Cu}_4\text{S}_4]^{3-}$  chains separated by sodium ions. Although there are two crystallographically distinct copper sites, both sites involve trigonal coordination by sulfur, with comparable Cu-S bond distances for the two copper ions. Thus, as in  $\text{KCu}_4\text{S}_3$ , there are no distinct Cu(I) and Cu(II) ions - e.g., the material is probably best described as delocalized class III-B mixed-valence compound.<sup>7</sup> We report here that the electrical properties of  $\text{Na}_3\text{Cu}_4\text{S}_4$  are totally consistent with this formulation.

## Experimental

Preparation of  $\text{Na}_3\text{Cu}_4\text{S}_4$ .  $\text{Na}_3\text{Cu}_4\text{S}_4$  was prepared as described in the literature.<sup>2,6</sup> Better crystals could be obtained by heating mixtures of copper powder, sulfur,

and sodium carbonate in a nitrogen atmosphere at approximately 500 - 550°C for 2 hours using a tube furnace. Anal. Calcd for  $\text{Na}_3\text{Cu}_4\text{S}_4$ : Na, 15.28; Cu, 56.31; S, 28.41. Found: Na, 15.90; Cu, 56.16; S, 27.96. Sodium was analyzed by atomic absorption spectroscopy, and copper was analyzed by EDTA titration using murexide indicator following decomposition in aqua regia. Sulfur determinations were performed by Schwarzkopf Analytical Laboratories.

Diffuse Reflectance. Samples were finely ground and dispersed in MgO. Diffuse reflectance spectra were measured using a Perkin Elmer 330 spectrophotometer equipped with a reflectance attachment using MgO as the reference.

Magnetic Susceptibilities. Magnetic susceptibilities of randomly oriented crystals were measured as described previously<sup>8</sup> using a conventional Faraday balance calibrated with  $\text{Hg}[\text{Co}(\text{NCS})_4]$ .<sup>9</sup> Diamagnetic corrections for the constituent atoms were made using values tabulated by Mulay.<sup>10</sup>

Electrical Conductivity. Four-probe DC conductivities of polycrystalline compactions were measured using the van der Pauw technique.<sup>11</sup> Pellets (6.3 mm diameter, typically 1 mm thick) were generally pressed at ca. 80000 psi, although measured conductivities were not sensitive to the pressure used in pellet preparation. A locally designed Teflon sample holder with four spring-loaded stainless-steel pressure contacts symmetrically disposed at the perimeter of the pellet was used for these measurements. Currents were imposed on a pair of adjacent probes using a Keithley Model 225 current source, and the voltage drop at the other pair of probes was measured using a Keithley Model 147 nanovoltmeter. A 90° rotation of the leads was used to insure that results were not sensitive to probe positioning. Conductivities were then calculated from the relationship



$$\sigma = \frac{\ln 2}{\pi t} \cdot \frac{I}{R} = 0.2206 \left[ \frac{I}{tV} \right]$$

where  $\sigma$  is the conductivity ( $\Omega^{-1} \text{cm}^{-1}$ ),  $R$  the resistance ( $\Omega$ ),  $I$  the imposed current,  $V$  the measured voltage, and  $t$  the pellet thickness (cm). Low temperatures were obtained by suspending the sample holder in the Faraday balance shroud of a Model CS-202 Displex closed-cycle helium refrigerator with a Model APD-E temperature controller manufactured by Air Products and Chemicals, Inc., Allentown, PA. Using this system measurements could be made from 13-300 K.

Single-crystal conductivity measurements at room temperature were made using both pressure contacts and silver paint contacts. In either case, electrical connections to the crystal were positioned using joy-stick micromanipulators manufactured by the Micromanipulator Co., Escondido, CA. Single-crystals for variable-temperature conductivity measurements were mounted in integrated circuit cans.<sup>12</sup> After grinding off the top of the can the crystal was attached to the central chip using double sided Scotch tape. Silver paint, prepared by diluting Dupont Conductor #4929 with hexyl acetate, was painted on the ends of the crystal and two thin strips of silver were painted across the crystal, approximately one-third of the way from each end. Connections to the integrated circuit terminals were achieved by painting a silver ribbon to the crystal contacts. Current was imposed through the outer contacts and the voltage drop measured between the inner two contacts. Crystal dimensions and voltage probe separations were measured by microscopic comparison to the scale of a hemacytometer counting stage which was ruled to 0.02 mm. Conductivities were calculated from the relationship  $\sigma = \frac{l}{A} \left( \frac{I}{V} \right)$  where  $l$  is the voltage probe separation,  $A$  the cross-sectional area of the crystal, and  $I$  and  $V$  the current and voltage respectively. Variable temperature measurements were made by suspending the integrated

circuit can in the shroud of the closed-cycle helium refrigerator, as described above for the compaction measurements. Ohmic behavior was verified in all cases.

### Results and Discussion

The original preparation<sup>2</sup> of  $\text{Na}_3\text{Cu}_4\text{S}_4$  involved placing sodium carbonate, copper, and sulfur in a double crucible arrangement and heating in a muffle furnace to 700 - 1000°C for 1-3 hours. Minute crystals of the compound are formed in this way, but alterations in both the relative amount of reactants and the reaction conditions seemed to have no consistent effect upon the quality of the crystals produced. We have found that significantly larger single crystals - necessary for the conductivity measurements - may be formed by carrying out the reaction in an inert atmosphere ( $\text{N}_2$ ) in a tube furnace at somewhat lower temperatures (ca. 550°C). Temperature control is rather important. If the reaction temperature is less than 500°C, the product is frequently contaminated by CuS. The presence of CuS may be detected visually, since it crystallizes as blue plates rather than the blue-black needles of  $\text{Na}_3\text{Cu}_4\text{S}_4$ . It is further reflected in the analytical results (high % Cu) and the room temperature conductivity (higher than that of  $\text{Na}_3\text{Cu}_4\text{S}_4$  by a factor of ca. 10). Higher reaction temperatures generally give pure  $\text{Na}_3\text{Cu}_4\text{S}_4$ , but as a powder rather than as crystals. This behavior contrasts with that observed in analogous preparations using potassium or lithium salts in place of sodium carbonate. Reactions using  $\text{K}_2\text{CO}_3$  produce CuS as the high (>1000°C) temperature product, whereas the reactions with  $\text{Li}_2\text{CO}_3$  give  $\text{Cu}_{1.8}\text{S}$  as the only identifiable copper sulfide.<sup>13</sup>

Although crystals of  $\text{Na}_3\text{Cu}_4\text{S}_4$  are apparently stable if stored in dry oxygen or under water, in moist air they slowly lose their metallic luster and develop an insulating surface coating. Consequently, all measurements reported here were made on fresh preparations of the material which had

been stored in a nitrogen atmosphere.

In the temperature range of 100-300 K,  $\text{Na}_3\text{Cu}_4\text{S}_4$  exhibits a temperature independent paramagnetism of ca.  $150 \times 10^{-6}$  emu/mole. This value is comparable to that found for  $\text{KCu}_4\text{S}_3$ , and is the behavior expected for a metallic system.<sup>14</sup> Below 100 K the compound exhibits Curie-like behavior, presumably as a consequence of the presence of a small amount of paramagnetic impurity.

The electrical conductivity for pressed pellets of  $\text{Na}_3\text{Cu}_4\text{S}_4$  has been measured using the four-probe van der Pauw technique.<sup>11</sup> For samples which we believe to be free of CuS contamination, the room temperature conductivity is consistently near  $300 \Omega^{-1}\text{cm}^{-1}$ . Thus, for five separate preparations which gave both the correct crystal morphology and copper analyses, the range of conductivity values was  $290 - 350 \Omega^{-1}\text{cm}^{-1}$ , with an average  $\sigma = 328 \pm 35 \Omega^{-1}\text{cm}^{-1}$ .

Rudorff, et.al.,<sup>2</sup> reported pressed pellet room temperature electrical conductivities of  $80 \Omega^{-1}\text{cm}^{-1}$  for  $\text{Na}_3\text{Cu}_4\text{S}_4$ ,  $70 \Omega^{-1}\text{cm}^{-1}$  for  $\text{K}_3\text{Cu}_8\text{S}_6$ , and  $40 \Omega^{-1}\text{cm}^{-1}$  for  $\text{KCu}_4\text{S}_3$ . By contrast, we find values of  $4000 \Omega^{-1}\text{cm}^{-1}$  for  $\text{KCu}_4\text{S}_3$ <sup>5</sup> and  $300 \Omega^{-1}\text{cm}^{-1}$  for  $\text{Na}_3\text{Cu}_4\text{S}_4$ . Although not stated explicitly, it is probable that Rudorff, et.al. use a two-probe measurement technique. In that case, the measured resistance is the sum of the inherent sample resistance plus the contact resistance. For such highly conducting materials, the contact resistance will dominate. Thus the low values for the conductivity which were reported, as well as the lack of differentiation among the various compounds, may be understood as the consequence of a two-probe measurement technique.

The temperature dependence of the pressed pellet conductivity is that of a metal. Upon cooling the sample (Figure 1) the conductivity increases

monotonically, reaching values of ca  $1500 \Omega^{-1} \text{cm}^{-1}$  at 15K. This increase - a factor of ca 4-5 - is rather small. We believe that it is not an inherent property of the compound, but rather an artifact caused by the use of pressed pellets. Interparticle contact resistances may represent a significant contribution to the total resistance for pressed pellets. To the extent that these terms are independent of temperature, they will mask the true dependence of the sample conductivity upon temperature.

$\text{Na}_3\text{Cu}_4\text{S}_4$  is structurally a pseudo one-dimensional compound,<sup>6</sup> and its electrical properties should be correspondingly anisotropic. Consequently, we have measured the conductivity of single crystals of  $\text{Na}_3\text{Cu}_4\text{S}_4$ . The crystals are needle-like, with a typical length of 1 mm and rectangular cross section  $0.03 \times 0.04 \text{ mm}^2$ . Because of these small dimensions, it has only been possible to measure the conductivity parallel to the needle axis, which corresponds to the direction of the one-dimensional  $[\text{Cu}_4\text{S}_4^{3-}]_\infty$  columns. Although crystal dimensions were estimated by optical comparison to a scale ruled to 0.02 mm, the small size of the crystals means that there is a relatively large uncertainty in these measurements. Since the calculation of the conductivity depends upon the cross-sectional area of the crystal, there will be a relatively large uncertainty in the absolute value of the single crystal conductivity. For ten separate crystals from two different preparations the average single-crystal conductivity was  $\sigma_{||} = 15200 \pm 3000 \Omega^{-1} \text{cm}^{-1}$ . The range for six crystals from one preparation was  $12500 \Omega^{-1} \text{cm}^{-1}$  to  $18700 \Omega^{-1} \text{cm}^{-1}$ , and we attribute this rather large spread to the difficulty in measuring the crystal dimensions precisely.

As for the pressed pellets, the temperature dependence of the conductivity of single crystals (Figure 2) is that of a metal, the conductivity increasing smoothly as the temperature decreased. In this case, however, the curve is steeper, and the conductivity increases by a factor of ca. 20 (from

15000 to 300000  $\Omega^{-1} \text{ cm}^{-1}$ ) upon cooling from 300 K to 15 K. This tends to substantiate our suggestion that the gentle temperature dependence observed with pressed pellets results from interparticle resistance.

These data demonstrate that  $\text{Na}_3\text{Cu}_4\text{S}_4$  is a pseudo one-dimensional metal. The single crystal conductivity parallel to the one-dimensional columns of the crystal is greater, by a factor of approximately fifty, than the bulk conductivity. Such a difference is common for low-dimensional materials, and is a reflection of both the inherent anisotropy of the material and the interparticle resistance in the pressed pellet measurements. The conductivity can not be strictly described as one-dimensional, since there is presumably finite electron mobility in all directions, although it would extend for only atomic dimensions perpendicular to the column axis. These columns are separated from each other by insulating regions occupied by sodium ions, and consequently on the macroscopic level the conductivity will be significantly anisotropic.

The plot of conductivity vs. temperature for both single crystals and pressed pellets of  $\text{Na}_3\text{Cu}_4\text{S}_4$  exhibits an apparent inflection point at ca. 40 K, and there is some suggestion that the conductivity will level off below the minimum temperature (13 K) accessible to us. Nonetheless, above ca. 80 K plots of resistivity vs. temperature are linear (Figure 3). This is behavior typical of simple metals, and may be contrasted to the case of molecular metals where the resistivity varies approximately as the square of the temperature.<sup>14</sup> Attempts to model the data using an equation of the form  $\rho = A + BT^2$  did not lead to acceptable agreement between calculated and experimental values.

A large number of copper sulfide phases are known,<sup>5</sup> including the obviously mixed-valence compounds  $\text{Cu}_{2-x}\text{S}$ . Although a range of stoichiometries are apparently possible, the discrete phases  $\text{Cu}_2\text{S}$  (chalcocite),  $\text{Cu}_{1.96}\text{S}$  (djurleite),  $\text{Cu}_{1.8}\text{S}$  (digenite), and  $\text{Cu}_{1.75}\text{S}$  (anilite) have been recognized.

Even CuS, which is nominally a simple Cu(II) compound, is mixed-valent, since discrete  $S_2$  groups (formally  $S_2^{2-}$ ) are present. Wells<sup>15</sup> has formulated this compound as  $Cu_4^I Cu_2^{II} (S_2^{2-})_2 (S^{2-})_2$ . Several of these phases exhibit metallic, or semi-metallic, electrical behavior.

$Na_3Cu_4S_4$  has Cu-Cu distances<sup>6</sup> which satisfy the Goodenough criterion<sup>16</sup> for high mobility collective electrons. The mixed-valence nature of this compound will lead to partially filled bands, and in consequence the high metallic conductivity seems explicable. Although  $Na_3Cu_4S_4$  has two distinct Cu sites, both involve trigonal coordination by sulfur with very similar bond distances. Clearly, there is no way to attribute these sites to distinct oxidation states of Cu, and  $Na_3Cu_4S_4$  is appropriately described as a Robin and Day Class III B mixed-valence compound. In this basis alone its metallic conductivity may be predicted. Similarly, although there are two crystallographically distinct sulfur sites, their environments are comparable and, to a first approximation, may be considered equivalent.

Although we have described these mixed-valence compounds as Cu(I,II) species, there is recent evidence that suggests that the mixed-valency resides in the sulfur rather than copper. In particular, x-ray photoelectron spectroscopy has demonstrated that all known copper sulfides - including  $KCu_4S_3$  and  $Na_3Cu_4S_4$  - contain Cu(I) only, with no evidence for either Cu(II) or intermediate oxidation states.<sup>17,18</sup> Thus, Folmer and Jellinek<sup>7</sup> reformulate CuS as  $Cu_3^+(S_2)^{2-}S^-$  and  $KCu_4S_3$  as  $K^+Cu_4^+(S_2^{2-})_2S^-$ . Using this scheme,  $Na_3Cu_4S_4$  must then be formulated as  $Na_3^+Cu_4^+(S^{2-})_3S^-$ . Because of the low electronegativity of sulfur and the relatively high electronegativity of copper, the copper d-levels fall within the valence band of sulfur. This results in a reduction of  $Cu^{+2}$  and  $Cu^{+1}$  with a concurrent partial depopulation of the sulfur valence band.<sup>19,20</sup> It is this partially filled valence band - formally mixed-valence sulfur - which is responsible for the metallic

conductivity of  $\text{Na}_3\text{Cu}_4\text{S}_4$ . Although this recent work emphasizes that it is necessary to describe these complexes differently (that is, as mixed-valence sulfur compounds rather than as mixed-valence copper compounds), it does not alter any fundamental conclusions. These are still Class III B mixed-valence compounds, with no distinguishable " $\text{S}^{2-}$ " and " $\text{S}^-$ " sites, and as such are expected to exhibit metallic conductivity.

Diffuse reflectance spectra of  $\text{Na}_3\text{Cu}_4\text{S}_4$  are consistent with this formulation. The spectra exhibit a reflectivity peak near  $35000\text{ cm}^{-1}$ , a very broad shoulder around  $20000\text{ cm}^{-1}$ , and a smeared out edge at  $12\text{--}14000\text{ cm}^{-1}$  which might be ascribed to the plasma edge. A reflectivity peak, ascribable to the  $3d \rightarrow 4s$  transition of Cu(I), often appears near  $35000\text{ cm}^{-1}$  in Cu(I) complexes. The observation of such a peak in  $\text{Na}_3\text{Cu}_4\text{S}_4$  supports the photoelectron spectroscopy work by suggesting that  $\text{Na}_3\text{Cu}_4\text{S}_4$  is a discrete Cu(I) complex.

A large number of alkali-copper-sulfide phases are now known, and it appears likely that all have interesting and unusual electrical properties. Furthermore, it appears that some of these materials are subject to chemical modification. We have, for example, prepared mixed Na/K analogs, but it is not yet clear whether these represent distinct phases or simply substitutional doping of  $\text{KCu}_4\text{S}_3$  and  $\text{Na}_3\text{Cu}_4\text{S}_4$ . We will report on other alkali copper sulfides at a later date.

Acknowledgement. This work was supported in part by the Office of Naval Research and by a NATO research grant. We are grateful to Dr. J.C.W. Folmer for providing us with a copy of his thesis.

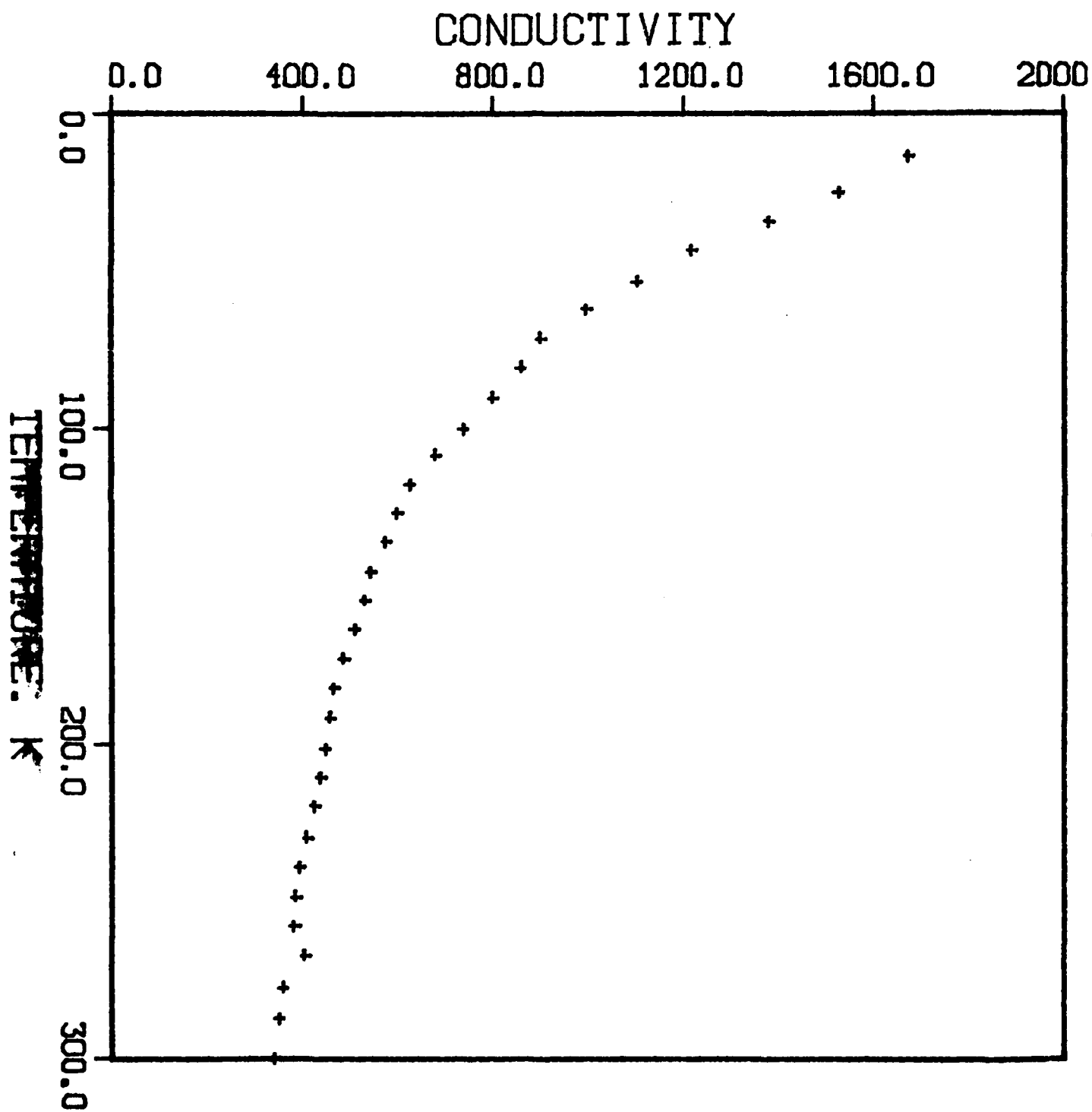
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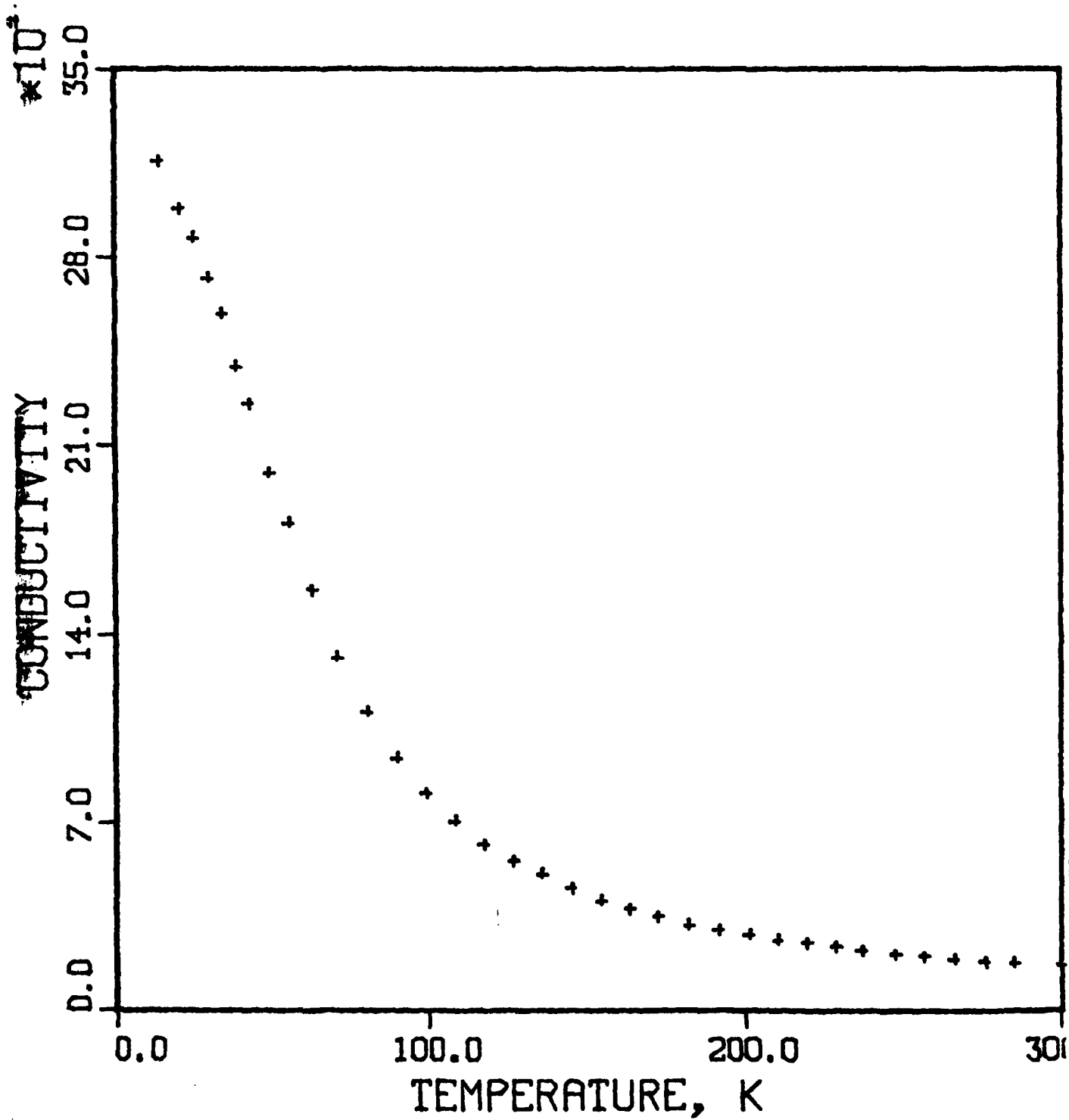
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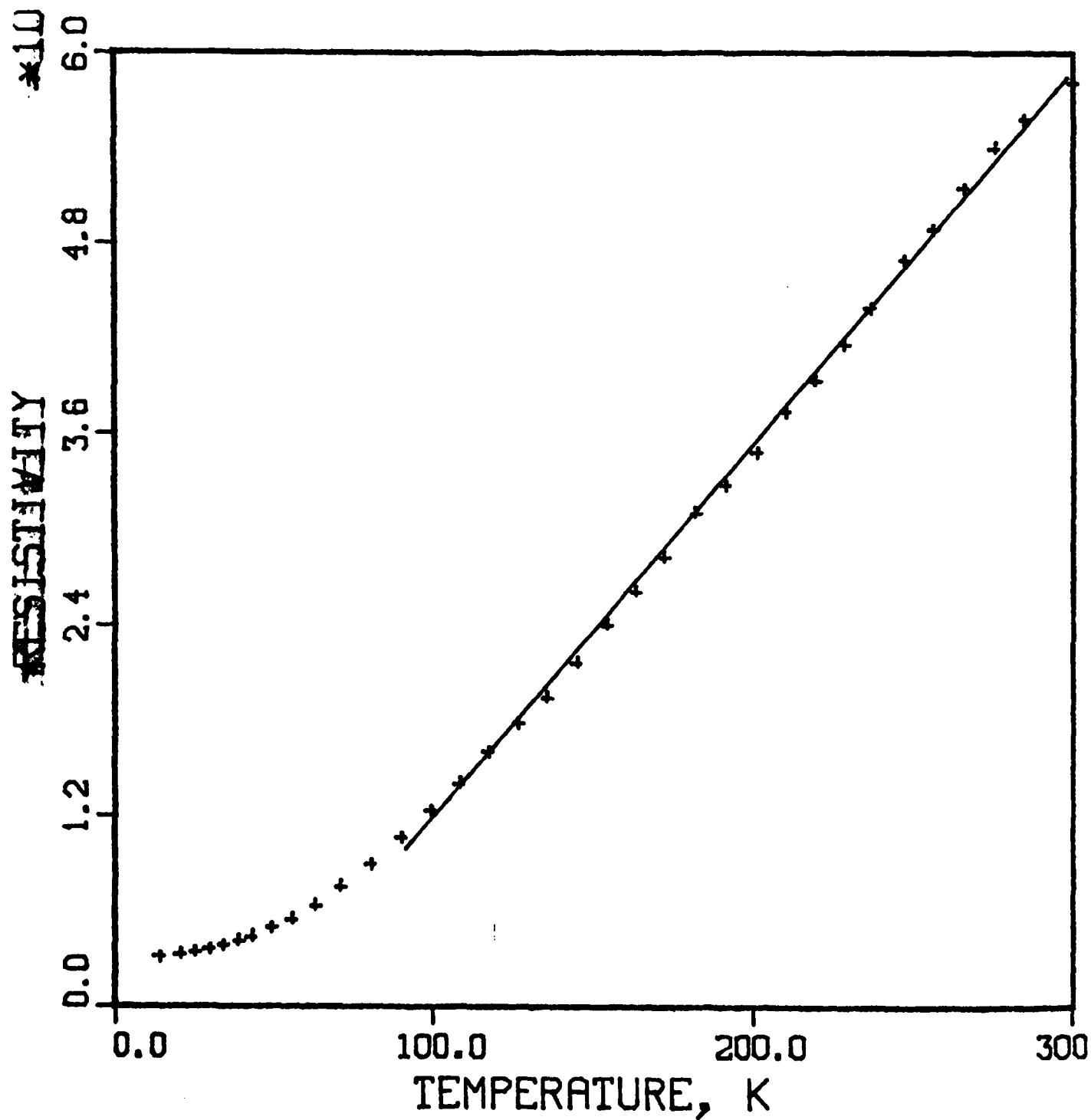


### Figure Captions

- Figure 1. Electrical conductivity ( $\Omega^{-1} \text{ cm}^{-1}$ ) as a function of temperature for a pressed pellet of  $\text{Na}_3\text{Cu}_4\text{S}_4$ .
- Figure 2. Electrical conductivity ( $\Omega^{-1} \text{ cm}^{-1}$ ) as a function of temperature for a single crystal of  $\text{Na}_3\text{Cu}_4\text{S}_4$ . Four-probe conductivities were measured parallel to the needle axis.
- Figure 3. Resistivity ( $\Omega \text{ cm}$ ) as a function of temperature for a single crystal of  $\text{Na}_3\text{Cu}_4\text{S}_4$ . The solid curve is the best straight-line fit to the data in the range 80-300 K.







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